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June 27, 2000

## BY EXPRESS MAIL

## BOX PATENT APPLICATION

Hon. Commissioner of Patents  
and Trademarks

Washington, DC 20231

Re: Application of R. David Prengaman, et al.

For: Electrowinning Anodes Which  
Rapidly Produce a Protective Oxide  
Coating

Our Ref.: 924150-EAW

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Theresa M. Gillis

(Name of person mailing correspondence)

(Signature of person mailing correspondence)

Sir :

We enclose the above-identified application for United States Letters Patent comprising

Abstract  
Specification (7 pages)  
Claims (16)  
Declaration  
Petition and Power of Attorney

Our check in the amount of \$690.00 is attached to cover the filing fee calculated as follows:

Basic Fee	\$690.00
Additional Fees:	
Number of independent claims in excess of three times \$78.00	0
Total claims in excess of twenty times \$18.00	0
<b>TOTAL FILING FEE</b>	<b>\$ 690.00</b>


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June 27, 2000  
Page 2

If there is any deficiency in the above-noted filing fee, kindly charge the amount of the deficiency against our deposit account no. **10-1202**. If there is an overpayment in the filing fee, kindly credit the amount of overpayment to the same deposit account.

Further, if during the prosecution of the accompanying application, there should occur any deficiency in the payment of the fees due, including claim fees occasioned by amendments, and in the payment of the issue fee or additional issue fee, please charge the amount of the deficiency against our deposit account.

Respectfully submitted,

  
\_\_\_\_\_  
Theresa M. Gillis  
Registration No 28,078

Enclosures

PETITION

TO THE COMMISSIONER OF PATENTS AND TRADEMARKS:



Your Petitioners,

1. **R. David Prengaman**, a citizen of the United States and a resident of Arlington, Texas, whose post office address is 2207 Ravinia Drive, Arlington, Texas, 76012,
2. **Clifford E. Morgan**, a citizen of the United States and a resident of Arlington, Texas, whose post office address is 2919 Forest Hollow Lane #2002, Arlington, Texas 76006,

pray that Letters Patent may be granted to them for their invention entitled **Electrowinning Anodes Which Rapidly Produce a Protective Oxide Coating**, set forth in the accompanying specification.

And we hereby appoint Thomas V. Heyman, Registration No 20,313, and Theresa M. Gillis, Registration No. 28,078, as our attorneys, with full power of substitution and appointment of associate attorneys, to prosecute this application and to transact all business in the Patent and Trademark Office connected therewith

Send all future correspondence to. Theresa M Gillis, Esq.  
Jones, Day, Reavis & Pogue  
599 Lexington Avenue  
New York, New York 10022

Signed at Dallas, Texas

this 23rd day of June, 2000

R. David Prengaman  
R. David Prengaman

Signed at Dallas, Texas

this 26 day of June, 2000

Clifford E. Morgan  
Clifford E. Morgan

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## ELECTROWINNING ANODES WHICH RAPIDLY PRODUCE A PROTECTIVE OXIDE COATING

This application is a continuation-in-part of Serial No 09/229,535, filed January 13, 1999,  
5 pending.

### Field of the Invention

This invention relates to an improved electrowinning anode particularly for zinc  
electrowinning. The anode consists of a rolled lead-silver alloy, preferably a lead-calcium-silver  
9 alloy, with controlled surface grain structure. Because the anode is used in zinc electrowinning,  
it should contain no tin. The surface grain structure is formed by a combination of anode  
chemistry, rolling and heating, preferably while rolling. When placed in a zinc electrowinning cell,  
the anode surface is rapidly covered with an adherent oxide coating.

### Background of the Invention

A zinc electrowinning tankhouse uses cast lead-silver alloy anodes. Silver is added to  
lead anodes for electrowinning to reduce the rate of corrosion of the anodes in use. Lead anodes  
used in zinc electrowinning generally contain 0.5-1.0% silver. Lead-silver anodes used for zinc  
electrowinning contain no tin because tin will plate on the negative anode and prevent zinc  
deposits.

To produce good quality zinc the cathode in an electrowinning cell must contain less than  
21 10 ppm lead. In order to reduce lead contamination of the cathode, the lead anode must be  
coated with a protective layer of  $PbO_2/MnO_2$ . The silver present in the anode decreases the rate  
of initial oxidation of the anode surface leading to an extended time period before a stable oxide  
film is produced. Conditioning new anodes by developing a  $PbO_2/MnO_2$  layer on the surface  
25 normally takes many weeks. The complete formation of this layer may take as long as 60-90

1 days. Until the anode is fully conditioned, the zinc cathodes in electrowinning cells experience  
high lead contents, high numbers of nodules and poor current efficiency. In addition, zinc  
production is substantially reduced as manganese ions are recirculated between anode and cathode  
as  $\text{MnO}_2$  spalled off the anode is reduced at the cathode to produce  $\text{MnSO}_4$ . The production of  
5 zinc from a cell containing new unconditioned anodes may produce as much as one-third less zinc  
than corresponding conditioned cells.

Once a stable layer of  $\text{PbO}_2/\text{MnO}_2$  is formed on the anode, the current efficiency of the  
zinc electrowinning process increases dramatically, and the lead contamination of the resultant  
cathodes also decreases dramatically. Production of a stable  $\text{PbO}_2$  or  $\text{PbO}_2/\text{MnO}_2$  layer via  
pretreatment of the anode is described by Ecgett *et al.* in U S Patent No 3,880,733, Gaunce *et*  
*al.* in U.S. Patent No. 3,392,094, Fountain *et al.* in U.S. Patent No 3,755,112, as well as R H  
Farmer in "Electrometallurgy" ed H Baker 1969 As described therein, a stable  $\text{PbO}_2$   
layer/ $\text{MnO}_2$  layer is typically created by the immersion of the anodes in a preconditioning solution  
in which the anodes are electrolyzed to produce corroded layers. In some cases the anodes are  
first immersed in water or water and air to produce a  $\text{PbO}$ ,  $\text{Pb}(\text{OH})_2$ , or  $\text{PbCO}_3$  film which is more  
readily oxidized to a protective  $\text{PbO}_2$  layer than the normal cast or rolled surface. Rodrigues and  
17 Meyer, in "EPD Congress 1996" ed G Warren, describe the use of sandblasting to aid in  
preconditioning anodes.

Lead-silver alloy anodes are relatively weak In use, they can become warped and bent  
leading to short circuits between the anode and cathode, low current efficiency, and lead  
21 contamination of the cathodes in the area of the short circuit To improve the mechanical  
properties of the lead-silver anodes alloying elements such as calcium, strontium, barium and  
others have been added to the anodes to improve the mechanical properties. For example, UK

1 patent application GB 2149424A by M.J. Thom teaches an alloy containing 0.4-1.0% Ag, 0.05-  
0.15% Ca/Sr, less than 0.0002% antimony and optionally barium to reduce calcium losses during  
remelting.

5 Production of cast lead-silver or lead-silver-calcium anodes often results in the formation  
of numerous holes, voids or laps in the anode surface. In use, these can initiate internal corrosion  
in localized areas which can weaken the anode and cause warping. When the anodes are  
periodically cleaned of the adhering  $\text{MnO}_2$  deposit, the internal corrosion may cause cracking  
which can lead to premature anode failure.

9 To reduce the presence of internal porosity or laps, lead-silver or lead-calcium-silver alloys  
have been rolled into sheets. These sheets have been joined to a copper busbar by various means  
but primarily by welding the rolled sheet to lead which has been cast around the copper busbar.  
The rolled sheet generally has a smooth surface on which it is more difficult for the  $\text{PbO}_2/\text{MnO}_2$   
corrosion product to produce an adherent film. In addition, the grain structure is uniform and is  
oriented in the rolling direction producing a grain structure with few grain boundaries available  
for corrosion and attachment of the oxidized film.

17 The improvement taught by this invention is the rolling of a cast billet of lead-silver alloys  
and treatment of the alloy during or after rolling at a temperature sufficiently high to produce a  
surface on which the  $\text{PbO}_2/\text{MnO}_2$  layer more readily adheres due to a grain structure having many  
grain boundaries. The grain structure is nonuniform (*i.e.*, not oriented in the rolling direction).  
These anodes have more satisfactory mechanical characteristics than prior art cast anodes and can  
21 be conditioned much more rapidly than prior art rolled anodes.

## Summary of the Invention

This invention relates to a lead-silver anode for zinc electrowinning having a randomly oriented grain structure with many grain boundaries. The anode is formed by rolling a cast lead-silver alloy and heat treating the alloy either during or after rolling at a temperature sufficiently high to cause recrystallization of the alloy and to prevent most or all of any calcium, barium and/or strontium present in the alloy from precipitating from solution. Because the anode is used for zinc electrowinning it contains 0% tin. In anodes formed via this procedure, finely divided silver particles form during solidification and prevent gross grain structure growth while the high temperatures result in a material with a recrystallized grain structure with many grain boundaries. The material is also without stresses induced by rolling. A temperature greater than about 100°C and preferably above about 150°C is typically required to produce the proper grain structure.

## Detailed Description of the Invention

In accordance with the invention, a lead-silver anode containing 0% tin for use in zinc electrowinning is formed preferably by rolling a cast lead-silver alloy at a temperature high enough to cause recrystallization of the alloy. The temperature is also high enough to prevent precipitation of any alloying elements, such as barium, calcium or strontium, during the rolling process. As a result, an alloy is formed having a grain structure with many grain boundaries to which the PbO<sub>2</sub>/MnO<sub>2</sub> layer may adhere more readily than in prior art alloys rolled at lower temperatures.

A lead alloy suitable for use in the practice of the invention may contain as little as about 0.30-0.45% silver. A preferred alloy also contains no more than about 0.08% calcium and preferably at least 0.03% calcium. A more preferred alloy contains about 0.04-0.07% calcium.

1 and about 0.3 to 0.5% silver, most preferably about 0.065% calcium and about 0.35% silver. The  
alloy may contain other alloying elements, including barium, strontium and other materials which  
enhance the mechanical properties of an anode. The alloy may also contain small amounts of  
aluminum to reduce the oxidation of the reactive alloying elements. The alloy must not contain  
5 any tin as tin will prevent zinc from depositing.

If the silver content of the lead alloy used to make the anode of the invention is too low,  
there are insufficient silver particles to restrict the growth of the grains during the hot rolling  
process. If the silver content is too high, the cost of the alloy is excessive.

9 If the calcium content of the lead alloy is too low, the improved mechanical properties  
attributable to calcium will not be achieved. If the calcium content of the invention is higher than  
about 0.08%, primary  $Pb_3Ca$  particles may precipitate from solution during the solidification  
process and float to the surface of the billet. This will result in an enrichment in calcium on one  
13 side of the rolled anode sheet compared to the remainder of the sheet. During use the side  
enriched in calcium will corrode preferentially causing warping, short circuits, reduced current  
efficiency and lead contamination of the cathode. The higher the calcium content of the anode  
above 0.08%, the higher is the differential rate of corrosion between faces and the more likely  
17 warping will occur in these rolled anodes.

If a billet is cast in a book mold prior to rolling from an alloy containing a calcium content  
higher than 0.08%, the primary  $Pb_3Ca$  particles will form a layer near the center line. During  
rolling the layer of particles will form a concentrated seam of calcium rich particles at the center  
21 of the sheet. When the sheet is cut and assembled into anodes, the high calcium content central  
areas will corrode preferentially causing delamination and fanning of the edges of the anode sheet.  
These defects can cause short circuits as well as lead contamination of the cathode.



1 With calcium contents between about 0.03 and 0.08%, all the calcium remains in solution during the solidification process and the billet has a uniform calcium content throughout. Rolling this material at the preferred temperature produces a uniform grain structure consisting of silver particles in a matrix of lead and calcium.

5 An alternative method of forming the anode of the invention consists of cold rolling the cast alloy. The cold rolled anodes are treated by heating to a temperature of about 150°C or above. Heating removes the effects of the cold rolling and produces a grain structure on which a stable oxide film can be formed rapidly. If an anode sheet containing calcium is rolled below  
9 100°C (cold rolling), some of the calcium can precipitate during the rolling operation. This precipitation, when combined with the silver content of the anode, can produce work hardening of the sheet. The hardened sheets can warp when some of the cold work is removed at tankhouse temperatures. Heating the anode sheet to a temperature above 150°C before use reverses the effects of calcium precipitation and the effects of cold rolling.

13 The grains of alloy sheets formed in accordance with the invention are randomly oriented instead of being oriented in the rolling direction, as is the case with prior art rolled alloys. This random orientation of fine grains with many grain boundaries presents a large grain boundary  
17 surface area in all regions of the surface. When an anode incorporating the rolled alloy is oxidized to produce a  $\text{PbO}_2/\text{MnO}_2$  layer, the oxidation is preferential to the grain boundaries and the  $\text{PbO}_2/\text{MnO}_2$  product attaches itself to these grain boundaries and rapidly covers the adjacent surface. Therefore, the anodes of the present invention can be much more rapidly conditioned  
21 than prior art anodes.

## Example

A lead-0.06% Ca-0.35% Ag alloy billet was hot rolled in a manner such that the temperature of the cast billet remained above 150°C during the rolling process. Sheets were attached to copper busbars via the process described by U.S. Patent No. 5,172,850. The resultant anodes were added as a full cell to a zinc electrowinning tankhouse. The anodes developed an adherent layer of  $\text{PbO}_2/\text{MnO}_2$  within two days and produced high current efficiency and low cathode lead contents from the first week of operation.

## Claims

What is claimed is:

1. An anode for electrowinning zinc comprising a rolled lead-silver alloy containing greater than 0% of a member selected from the group consisting of calcium, barium and strontium, containing 0% tin and having a randomly oriented grain structure.
2. The anode of claim 1 in which the alloy is a lead-calcium-silver alloy.
3. The anode of claim 2 in which the calcium content is below 0.08%
4. The anode of claim 2 in which the calcium content is between 0.03 and 0.08%
5. The anode of claim 2 in which the silver content is at least 0.3%
6. The anode of claim 2 in which the silver content is between 0.3 and 0.5%.
7. The anode of claim 2 in which the calcium content is between 0.04 and 0.07% and the silver content is between 0.3 and 0.4%.
8. The anode of claim 2 in which the calcium content is about 0.06% and the silver content is about 0.35%.
9. The anode of claim 1 in which the rolled alloy is attached to a copper busbar
10. The anode of claim 1 in which the alloy contains barium
11. The anode of claim 1 in which the alloy contains strontium
12. A lead-silver alloy for electrowinning zinc containing greater than 0% of a member selected from the group consisting of calcium, barium and strontium, containing 0% tin and having a randomly oriented grain structure which is not corrosion resistant
13. An anode for electrowinning zinc formed by rolling a lead-silver alloy containing greater than 0% of a member selected from the group consisting of calcium, barium and strontium and 0% tin, and heat treating the alloy at a temperature sufficiently high to cause



An anode for use in zinc electrowinning is described. The anode is made of a lead-silver alloy which has been cast as a billet, rolled and subjected to heat treatment either during or after rolling. The temperature of treatment is high enough to cause recrystallization of the alloy and to prevent precipitation of any alloying elements. The anode has a surface grain structure which facilitates rapid oxidation of the anode to condition the anode. The anode preferably contains at least 0.03 to 0.45% silver and up to 0.08% calcium.

## DECLARATION FOR PATENT APPLICATION

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name.

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled:

### ELECTROWINNING ANODES WHICH RAPIDLY PRODUCE A PROTECTIVE OXIDE COATING

the specification of which is attached hereto.

I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose information which is material of the examination of this application in accordance with Title 37, Code of Federal Regulations, Section 1.56(a).

I hereby claim foreign priority benefits under Title 35, United States Code, Section 119 of any foreign application(s) for patent or inventor's certificate listed below and have also identified below any foreign application for patent or inventor's certificate having a filing date before that of the application on which priority is claimed.

Prior Foreign Application(s)

Priority Claimed

Number \_\_\_\_\_ Country \_\_\_\_\_ Yes \_\_\_\_ No \_\_\_\_

Day/Month/Year Filed \_\_\_\_\_

Number \_\_\_\_\_ Country \_\_\_\_\_ Yes \_\_\_\_ No \_\_\_\_

Day/Month/Year Filed \_\_\_\_\_

Number \_\_\_\_\_ Country \_\_\_\_\_ Yes \_\_\_\_ No \_\_\_\_

Day/Month/Year Filed \_\_\_\_\_

I hereby claim the benefit under Title 35, United States Code, Section 120 of any United States application(s) listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States application in the manner provided by the first paragraph of Title 35, United States Code, Section 112, I acknowledge the duty to disclose material information

as defined in Title 37, Code of Federal Regulations, Section 1.56(a) which occurred between the filing date of the prior application and the national or PCT international filing date of this application:

Application Serial No.: 09/229,535 Filing Date 01/13/99

Status: Pending

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

\* \* \*

Full name of sole or first inventor

**R. David Prengaman**

Inventor's signature R David Prengaman

Date: June 23,, 2000

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Full name of second joint inventor, if any.

**Clifford E. Morgan**

Inventor's signature Clifford E. Morgan

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